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#### A B S T R A C T

There is provided a rapid method for the preparation of crosslinked starch wherein the original starch granule shape has been preserved. The method involves carrying out cross-linking reaction at a temperature and a sodium hydroxide concentration which are above gelatinization level. This process reduces the reaction time to one to two hours as compared with fifteen to twenty-five hours by prior art methods. The cross-linked starch can also be etherified within a very short period of from 0.5 to 2 hours to provide an etherified starch product.

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This invention relates to a rapid method for preparation of crosslinked starch and starch derivatives wherein the original starch granule shape has been preserved. Further these derivatives are characterized by improved resistance of their aqueous dispersions to loss of hydrating capacity, and loss of clarity and texture upon aging at low temperatures or upon repeated freezing and thawing. Similar improvement in stability to heat and chemical treatment is found in these materials compared to conventional starch.

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PRIOR ART

Starches have traditionally been used in the food industry as ingredients which have nutritive value and which can at the same time impart functional properties to food systems. Depending upon the type used modified starches may serve to facilitate processing, provide texture, thicken, suspend solids, or protect food during processing, distribution and storage. In a few cases unmodified starches may be used, but in many instances modified starches are preferred because they are more versatile and will perform functions which cannot be handled with unmodified types.

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The starch granules are composed of linear and branched molecules associated by hydrogen bonds either directly or through water hydrate bridges to form radially oriented micelles or crystalline areas of various degrees of order. An interconnected three-dimensional micellar lattice is formed by the participation of segments of individual molecules in several micellar areas. The overall strength of the micellar network (which is itself dependent on the degree of association and the molecular arrangement) controls the behaviour of starch in water.

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Starch granules exhibit a limited capacity for



absorbing cold water and swelling reversibly. Thus the inter-micellar network must possess a limited degree of elasticity. The subjection of an aqueous suspension of starch to the influence of heat or appropriate chemicals weakens the micellar network within the granules by disrupting hydrogen bonds. This permits further hydration and irreversible granule swelling, a process termed gelatinization. Fundamentally, the gelatinization of starch in various media is attributed to the chemical affinity of the starch molecules for the solvent. When starch

10 is gelatinized in an aqueous medium, the individual granules undergo a series of physical changes of which the most important is swelling. As is known, starch gelatinizes in aqueous suspension only at higher temperature. If an aqueous suspension of starch is heated, the granules do not change in appearance until a certain critical temperature is reached. At this point some of the granules swell radially and simultaneously lose their characteristic Maltese cross between crossed polaroids. The gelatinization temperature range varies with starch species. Normally the gelatinization temperature is not

20 affected by the presence of the linear starch fraction, and, hence normal and waxy starches of the same species usually gelatinize over the same temperature range.

The gelatinization temperature range is markedly altered by the addition of certain chemicals and by chemical modification of starch. Aqueous solutions of certain substances such as sodium hydroxide and other alkalies gelatinize starch at room temperature. The critical concentration level of alkali for example is dependent on the type of alkali and on the species of starch *H. W. Leach, T. J. Schoch and E. F.*

30 *Chessman Stacks 13,200 (1967)* and it lies between 0.32-0.4% by weight. Naturally, the cold gelatinization of starch in

aqueous alkali depends on the relative amounts of each of the three components present: water, alkali and starch. The individual granules adsorb alkali in accordance with the Freundlich adsorption equation and gelatinize when the amount of adsorbed alkali exceeds the critical concentration.

As mentioned above the resistance of starch to hot and chemical gelatinization is very strongly affected by chemical modification. Some of the most important modifications of starch seem to be etherification, esterification and cross-  
10 linking.

Such methods of modifying starch are described in U.S. Patent 2,935,510, O. B. Wurzburg, May 3, 1960 which describes a two-step method, in which the first step uses epichlorohydrin or phosphorous oxychloride as a crosslinking agent; and in the second step acetic or propionic anhydride is used for esterification. The reaction time extends over 15-20 hours at temperatures of 15-25°C.

In British Patent No. 1,199,090, Penick and Ford Limited, published July 15, 1970, which is also a two-step  
20 process, wherein divinylsulfone is used; and as etherification agents ethylene oxide, propylene oxide, 1,2 epoxy butane, sodium monochloroacetate, acrylonitrile, allyl chloride, methyl chloride and urea-formaldehyde resin solution (URAC) are used as crosslinking agents. The foregoing modified reactions are carried out in aqueous alkali solution at temperature ranges between 20-40°C. The serious disadvantage of this process is the long time necessary for the two-step modification, which ranges between 20-140 hours.

Starch modified by the above methods may be fully  
30 gelatinized under neutral pH conditions because the cross-linking bonds formed by divinylsulfone can be broken at pH 7.

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U.S. Patent No. 2,500,950, M. Konigsberg, March 21, 1950, discloses a method for preparing an inhibited starch, which resists gelatinization in aqueous suspension at high temperature and also resists gelatinization due to chemical treatment. In this method only crosslinking agents such as epichlorhydrin, dichlorhydrin, 1,5-dichlorbutane, ethylene dibromide, 1,4-dichlorbutane are used without an etherification agent. Also in this method the time of modification is very long: 16-24 hours.

10 U.S. Patent No. 3,437,493, J. W. Robinson et al, April 8, 1969, relates to a starch thickener prepared by using a granular phosphorous oxyhalide to crosslinked hydroxypropyl cereal starch or acetylated cereal starch. In the first step of this process the etherification of starch is carried out with propylene oxide in aqueous solutions of sodium hydroxide (conc. 0.87% per weight), while using 30% sodium sulfate as antigelatinization agent. In the second step crosslinking is carried out with phosphorous oxychloride. The total reaction time for both steps is 19 hours.

20 Another U.S. Patent No. 2,929,811 relates to preparation of modified starch material where in the first step epichlorhydrin is used as a crosslinking agent and in the second step sodium periodate and sodium chlorite are used. The total reaction time for both steps is 21-42 hours.

After a study of the prior art methods for preparing modified starch derivatives for the food industry it would appear that these methods suffer from the following main disadvantages.

30 First, the crosslinking reaction has to be carried out at very low concentration of 0.4 to 0.5% of sodium hydroxide at room temperature and therefore the reaction time is very

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long, varying between 16 to 25 hours. Secondly, if a somewhat higher concentration, for example 0.87%, of sodium hydroxide is used, or a higher temperature such as 40-60°C. it is necessary to use simultaneously a very high concentration of some electrolyte as antigelatinizing agent, for example about 20-30% of sodium sulfate per weight of starch, which must subsequently be removed. Thirdly, the modification reactions of starch are usually carried out in two steps. The first step involves the crosslinking reaction at room temperature and low concentration  
10 of sodium hydroxide. The crosslinking agent may be epichlorhydrin or another bifunctional crosslinking agent. In the second step the etherification reaction is carried out at a higher temperature and a higher concentration of sodium hydroxide. As etherification agent there is usually used ethylene oxide, propylene oxide, acrylonitrile, sodium monochloracetate or others. Also the etherification step requires a long period of time varying from 10 to 20 hours.

In accordance with the present invention there is now provided a novel method for crosslinking starch in a relatively  
20 short time. Although the reaction is performed at a temperature and a sodium hydroxide concentration which are above the gelatinization level nevertheless the modified starch products can be easily purified by washing with water without causing the starch to swell to a point where it cannot be filtered. Because it has been found possible to carry out the crosslinking reaction with higher concentrations of sodium hydroxide and at higher temperatures than normally used, the overall reaction time has been drastically reduced to 1 to 2 hours as compared to a reaction time of from 15 to 25 hours when using  
30 prior art methods.

The novel method of the present invention comprises

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first mixing starch with sodium hydroxide, concentration of which is below the gelatinization concentration, and with 0.1 to 2% by weight of starch of a crosslinking bifunctional compound of the formula: X-R-Z wherein R is an alkylidene radical containing from 3 to 10 carbon atoms which may be substituted by one or more hydroxyl radicals, and X and Z respectively stand for halogen and epoxy. After standing for a short period of time the spent alkali solution is separated from the starch, for example, by filtration or centrifugation, whereby there is  
10 obtained a wet starch containing from about 40 to 50% of solvent from 0.8 to 1.2% of sodium hydroxide and 0.05 to 2.0% of crosslinking agent calculated on the weight of dry starch. Because the sodium hydroxide and crosslinking agent are not removed by filtration their respective concentrations with regard to the weight of starch have been significantly increased and at this stage the overall sodium hydroxide concentration is above the gelatinization concentration, but due to the high solids concentration the suspension maintains its granular texture. The wet starch is then crosslinked by  
20 heating to a temperature of from 40 to 70°C. for a period of from 30 to 60 minutes.

The modified starch products produced in accordance with the present invention possess great commercial value because of their distinctively smooth and relatively non-cohesive character. They find value in foods such as salad dressings, puddings and pie fillings, and also in the textile industry as printing gums since their smooth and non-cohesive character is not adversely affected by alkalies found in  
30 certain textile printing operations. The starch products of the present invention find an important use in exclusion chromatography where controlled swelling of the starch granules



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which are easily obtained by the process of the present invention will allow different levels of molecular size exclusion. Finally, the simplicity of the process allows the use of chemically modified starches in many areas where ordinary starches have long been in use, for example, in adhesives.

It should be appreciated that the unexpected feature of the process of the present invention is to be able to carry out the crosslinking reaction of starch at a relatively high temperature and at a concentration of sodium hydroxide above the gelatinization level, even though concentration of starch as high as 55 to 65% by weight are used in the reaction mixture. It should also be appreciated that the concentration of sodium hydroxide which will cause gelatinization of starch is different for various types of starch and also depends on the ratio starch: reagent solution. It has been discovered that by proceeding accordingly and by working at high starch concentrations, gelatinization has been prevented.

Table I shows the bed volume dependence of various types of starch as a function of sodium hydroxide concentration for a ratio of starch: reagent solution of 1/10.

TABLE I

THE BED VOLUME OF STARCH SAMPLES IN AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE AT DIFFERENT LEVELS OF NaOH CONCENTRATION

| Starch sample | Bed volume of starch in ml/g       |      |     |     |      |     |     |
|---------------|------------------------------------|------|-----|-----|------|-----|-----|
|               | Concentration NaOH in % per weight |      |     |     |      |     |     |
|               | 0                                  | 0.1  | 0.2 | 0.3 | 0.4  | 0.6 | 0.7 |
| Potato starch | 1.6                                | 1.8  | 2.5 | 4.8 | 22.5 | ∞   | ∞   |
| Wheat starch  | 1.6                                | 1.7  | 2.0 | 2.6 | 4.8  | ∞   | ∞   |
| Corn starch   | 1.6                                | 1.65 | 1.7 | 1.8 | 2.0  | 19  | ∞   |

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From the results in Table I it can be concluded that the critical concentration of sodium hydroxide at a ratio: starch solution of 1/10 is about 0.3% for potato starch, 0.4% for wheat starch and 0.5% for corn starch. Naturally the cold gelatinization of starch in aqueous alkali depends on the relative amounts of each of the three components present: water, alkali and starch.

The adsorption of sodium hydroxide on the starch granules is a relatively rapid process, because the equilibrium is attained in 15 - 20 minutes as can be seen from the results in Table II.

TABLE II

ADSORPTION OF SODIUM HYDROXIDE ON POTATO STARCH FROM 0.35% SOLUTION OF SODIUM HYDROXIDE AS A FUNCTION OF STARCH TO SOLUTION RATIO

| Ratio<br>starch::solution | NaOH adsorption in % per weight of starch |      |      |      |
|---------------------------|---|------|------|------|
|                           | Time adsorption in min.                   |      |      |      |
|                           | 7   | 15   | 22   | 30   |
| 1 :: 1                    | 0.22                                      | 0.29 | 0.31 | 0.31 |
| 1 :: 3                    | 0.75                                      | 0.87 | 0.88 | 0.88 |
| 1 :: 5                    | 1.00                                      | 1.13 | 1.14 | 1.14 |
| 1 :: 10                   | 1.64                                      | 1.68 | 1.68 | 1.68 |

It is evident that adsorption of sodium hydroxide by starch from its aqueous solutions which are below the gelatinization concentration levels may be exploited to accelerate crosslinking and etherification reactions of starch. In this way, 0.3 - 1.2% of NaOH may be adsorbed on the starch without

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gelatinizing and it may then be easily separated by filtration or by centrifugation from the original solution.

As can be seen in Table III, the starch after filtration retains no more than 60 - 100% of solution on the weight of starch.

TABLE III

ANALYTICAL RESULTS FOR EXPERIMENTS INVOLVING SODIUM HYDROXIDE ADSORPTION ONTO  
STARCH AS A FUNCTION OF THE STARCH TO SOLUTION RATIO

| Ratio<br>starch: solution<br>at sorption in<br>0.36% NaOH | Solution retained<br>by starch after<br>filtration in % by<br>weight of starch | Concentration<br>of starch in<br>the retained<br>solution in % | Concentration<br>of NaOH in<br>the retained<br>solution in % | Concentration<br>of NaOH in<br>filtrate in % | Amount of<br>sorbed NaOH in<br>% per weight<br>of starch |
|---|--|--|--|--|--|
| 1 :: 1  | 61   | 62   | 0.56   | 0.04   | 0.31   |
| 1 :: 3  | 68   | 59   | 1.3  | 0.1  | 0.88   |
| 1 :: 5  | 82   | 55   | 1.4  | 0.14   | 1.14   |
| 1 :: 10   | 100  | 50   | 1.68   | 0.21   | 1.68   |

An important fact is that the concentration of sodium hydroxide in the solution retained by starch is 2 - 4 times higher than in the original solution. With increasing concentration of the sodium hydroxide the rate of the crosslinking reactions are greatly accelerated, hence the preferential adsorption can be used to advantage for this reaction.

10 The reason that the starch may be heated to higher temperature (50 - 70°C.) and at sodium hydroxide concentrations higher than the gelatinization level, is because of the deficit of solvent which has been separated by filtration or centrifugation from the starch before heating of the reaction mixture.

It is also interesting to note that the crosslinking agent, (preferably epichlorhydrin) is well adsorbed together with sodium hydroxide onto the starch. Under the same condition of adsorption, 96 - 98% of the epichlorhydrin used for crosslinking is absorbed on the starch. This is also an important fact because in this way a homogeneous distribution both of sodium hydroxide and consequently of crosslinking and other groups is assured in the modified starch.

20 After sorption of sodium hydroxide and epichlorhydrin onto the starch the granules are filtered or centrifuged to separate them from the liquor; at this stage, they are free flowing and have the consistency of alkali cellulose "crumb". They are then heated to a temperature of 40 - 70°C. without risk of gelatinization. Under these conditions the crosslinking of starch is over in 30 - 60 minutes, which is 10 - 15 times faster than in the other known methods. After crosslinking the resulting product is washed with water and dried by known operations.

30 Products based on modified starch prepared by the method of our invention are remarkably resistant to deterio-

ration upon exposure to prolonged cold and to heat or chemical treatment. The degree of resistance of starch to gelatinization is dependent on the amount of epichlorhydrin used in reaction. In this invention, we prefer an amount: 0.05 - 0.2% of epichlorhydrin on the weight of dry starch.

Suitable crosslinking agents are the bifunctional organic substances of the type X-R-Z wherein R is an aliphatic residue, containing 3-10 carbon atoms and X and Z are respectively halogen atom and an epoxy group, the latter being  
10 linked to carbon atoms of the aliphatic group to an oxirane ring. The aliphatic residue can contain substituents, preferably one or more hydroxyl groups and/or be interrupted by heteroatoms preferably oxygen atoms. As an example of suitable bifunctional substances there may be mentioned epichlorhydrin dichlorhydrin, bromohydrin 1,2 - 3,4 di-epoxybutane, bis-epoxy-propylether, 1,4 - butane-diol bis-epoxypropylether and other related compounds. As stated previously, the preferred cross-linking agent is epichlorhydrin.

In order to prevent the gelatinization of starch  
20 during the reaction in this invention it is very important to use the correct concentration of sodium hydroxide and to control the ratio of starch to aqueous alkali solution in the sorption step. These values depend on the starch type.

The optimal concentration of sodium hydroxide for a potato starch is about 0.35 - 0.38%, for wheat starch 0.4 - 0.45% and for corn starch 0.5 - 0.55% at ratio: starch solution of 1 1.5-2.0. Under these conditions about 0.8 - 1.2% of sodium hydroxide is adsorbed on the starch and simultaneously 95-97% of the epichlorhydrin which has been solved in the  
30 aqueous alkali solution used.

Under the conditions mentioned above, sorption

equilibrium is attained in 15 - 20 minutes and starch may easily be separated from the alkali solution by filtration or centrifugation. After filtration, the starch contains about 38 - 45% of the volume of aqueous solution, with 2 - 3 times higher NaOH concentration related to the original concentration of alkali solution used.

After separation of excess spent alkali solution the starch may be heated to higher temperatures, about 40 - 60°C., without risk of gelatinization of the starch granules. In this  
10 invention we prefer the temperature 50°C. at which temperature the crosslinking is over in 40 - 60 minutes and the resulting crosslinked starch product may be purified by washing with water and dried by known procedures. If besides crosslinking we want also to carry out some modification reaction on the starch, it may be done easily after finishing the crosslinking step.

A further feature of the present invention is that the crosslinked starch previously described can be subjected to an etherification reaction to provide starch which has been  
20 further modified.

Because the concentration of sodium hydroxide after crosslinking of the starch according to this invention, is relatively low for etherification reactions it is often necessary first to increase it. This may conveniently be done by spraying a high concentration solution of sodium hydroxide, to obtain an 8-20% concentration level in the reaction mixture. The final concentration level to be attained depends on the etherification reagent. Instead of spraying a high concentration solution of sodium hydroxide we prefer in our invention  
30 the adding of a solid powder of sodium hydroxide to the reaction product after the crosslinking step. In this way, the

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ratio of solvent to starch is not increased and it is possible to use a smaller amount of sodium hydroxide for attaining the same concentration of alkali needed for the etherification step of starch modification.

After homogenization of the crosslinked starch and NaOH mixture the etherification agent is added and temperature is increased to 40-60°C. (if necessary) and the etherification reaction is allowed to proceed. The reaction time for this step is usually about 0.5 - 2 hours. It is very important to  
10 note that the efficiency of the etherification reaction under the mentioned conditions is higher than in the known procedures because all side reactions of etherification agents are reduced by the high concentration of sodium hydroxide and by the low ratio of water to starch.

Etherification agents which may be used are: ethylene oxide, propylene oxide, sodium monochloracetate, acrylonitrile 2-chloro-N,N-diethyl-ethyleneamine hydrochloride and others.

The amount of etherification agent used in the modification step may be varied over a wide range but we prefer in  
20 this invention about 5 - 15% of etherification agent per weight of dried starch. For general application, we recommend use of an amount of etherification agent which is able to get the starch product to a degree of substitution (DS) about 0.05 - 0.1. When the etherification step of starch modification is over the resulting product: a crosslinked etherified starch derivative is purified by washing with water and dried according to known procedures.

The modified starch produced according to this invention is in the physical form of starch granules having the  
30 property of inhibited gelatinization when dispersed with water under normal gelatinization conditions. The degree of inhi-



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bition is dependent upon the nature and quantity of cross-linking reagent employed and upon the type and amount of etherification reagent used.

The more exact embodiment of preparing the modified starches by the method of the present invention will be apparent from the following examples which are illustrative of preferred embodiments of the present invention. It should be understood that these examples are not intended to limit the invention and obvious changes may be made by those skilled in the art without changing the essential characteristics and the basic concept of the invention.

The parts and percentages are by weight, the temperature is room temperature, and pressure is atmospheric, unless otherwise indicated.

#### EXAMPLE I

100 Parts of unmodified potato starch with normal water regain of 10-15% are suspended in 150 parts of 0.36% aqueous solution of sodium hydroxide, in which 0.5 parts of epichlorhydrin had been dissolved. The starch suspension is mixed at room temperature for 25 minutes, until the sorption of sodium hydroxide and epichlorhydrin in the starch granules is complete. The spent alkali liquor is then separated from starch by filtration or centrifugation. After filtration, the starch contains about 40% of water with 0.8% sodium hydroxide and 0.47% epichlorhydrin, the whole calculated on the weight of dried starch.

Wet starch with the mentioned adsorbed chemical agents is then heated to a temperature of 50°C. at which temperature the crosslinking of starch is over in 45 minutes. The resulting crosslinked starch is acidified by acetic acid and washed with water and dried by known procedures.

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The reaction product obtained is an inhibited potato starch which upon cooking in the ratio one part potato starch to fifteen parts of water, produces a relatively non-cohesive paste. The addition of several percent of sodium hydroxide to the cooked suspension causes further swelling of starch granules but does not destroy the non-cohesive character of the paste.

EXAMPLE II

10 The procedure of Example I is followed except that one part of epichlorhydrin is used. The resulting reaction product is a more gelatinization inhibited potato starch which does not revert to the dispersed state even upon prolonged contact with alkali at higher temperature.

EXAMPLE III

The procedure of Example I is followed except that the wheat starch and 0.45% concentration of sodium hydroxide were used. The resulting product: crosslinked wheat starch, has similar properties as the starch in Example I.

EXAMPLE IV

20 The procedure of Example I is followed except that the corn starch and 0.55% concentration of sodium hydroxide are used. The resulting crosslinked corn starch has properties similar to the starch in Example I.

EXAMPLE V

30 The procedure of Example I is followed except that the starch after crosslinking is not washed and dried but immediately five parts of solid powder sodium hydroxide is added (alternatively may be sprayed 10 ml. of 50% solution of sodium hydroxide) and the reaction mixture is mixed 30 minutes in order to get a homogeneous distribution of alkali on the starch. After homogenization of the reaction mixture seven

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parts of propylene oxide is added and at a temperature of 45°C. the hydroxypropylation of the starch is over in 60 minutes. The purified and dried product is crosslinked hydroxypropyl starch with a degree of substitution (DS) of about 0.1 - 0.15.

EXAMPLE VI

The procedure of Example I is followed except that the starch after crosslinking is not washed and dried but immediately ten parts of powdered sodium hydroxide is added simultaneously with fourteen parts of solid sodium monochlor-  
10 acetate and after 30 minutes of mixing the temperature of the reaction mixture is increased to 60°C. and at this temperature the carboxymethylation of starch is over in 60 minutes. The purified and dried product is crosslinked carboxymethyl starch with a degree of substitution (DS) about 0.1 - 0.15.

EXAMPLE VII

The procedure of Example I is followed except that the starch after crosslinking is not washed and dried but it is cooled to room temperature and eight parts of powdered sodium hydroxide is added and the reaction mixture is mixed 30  
20 minutes, in order to get a homogeneous distribution of sodium hydroxide. After homogenization, ten parts of acrylonitrile is added and the cyano ethylation is over at room temperature in 45 minutes. The purified and dried product is crosslinked cyanoethyl starch with a degree of substitution (DS) about 0.1 - 0.15.

EXAMPLE VIII

The procedure of Example I is followed except that, the starch after crosslinking is not washed and dried but immediately sixty parts of sodium-chloracetate and an emulsion  
30 of 64 ml of a 40% aqueous solution of sodium hydroxide and 30 ml epichlorhydrin were added. The temperature of the reaction mixture increases rapidly and after 10-15 min. attains 50-60°C.

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at which temperature the reaction is complete after 90 mins. After cooling the reaction product is washed and dried by known procedures.

The yield of dry product of crosslinked carboxymethyl starch with the preserved original starch granule structure is 140 g. The ion-exchange capacity of the product is 1.0 meg/g and the bed volume in water 5.0 ml/g.

EXAMPLE IX

10 The procedure of Example VIII is followed except that instead of sodium-monochloracetate 85 g 2-chloro-N,N-diethyl-ethylamine hydrochloride were used. The resulting product is a weakly basic anion-exchanger; diethyl-amino-ethyl starch, with preserved original starch granule shape and it has an ion-exchange capacity 1.3 meg/g and a bed volume 4.5 ml/g.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A rapid method for the preparation of crosslinked starch wherein the original starch granule shape has been preserved which comprises mixing starch with sodium hydroxide the concentration of which is below the gelatinization concentration and with 0.1 to 2% by weight of starch of a crosslinking bifunctional compound of the formula: X-R-Z wherein R is an alkylidene radical containing from 3 to 10 carbon atoms which may be substituted by one or more hydroxyl groups, and X and Z respectively stand for halogen and epoxy, allowing the mixture to stand for a short period of time, separating the spent alkali solution from the mixture whereby there is obtained a wet starch containing from about 40 to 50% of solvent, from 0.8 to 1.2% of sodium hydroxide, said amount being above the gelatinization concentration, and 0.05 to 2.0% of crosslinking compound calculated on the weight of dry starch, heating the wet starch to a temperature between 40° to 70°C. for a period of from 30 to 60 minutes thereby effecting crosslinking of the starch.

2. The method of Claim 1, wherein the crosslinking compound is epichlorhydrin.

3. The method of Claim 1, wherein the starting starch is potato starch and the initial concentration of sodium hydroxide is from 0.35 to 0.38%.

4. The method of Claim 1, wherein the starting starch is wheat starch and the initial concentration of sodium hydroxide is from 0.4 to 0.45%.

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5. The method of Claim 1, wherein the starting starch is corn starch and the initial concentration of sodium hydroxide is from 0.5 to 0.55%.

6. The process of Claim 1, wherein the sodium hydroxide concentration of the crosslinked starch obtained is adjusted to 8 to 20% and the mixture is reacted with an etherification agent for a period of time of from about 0.5 to about 2 hours until an etherified starch product having a degree of substitution of from 0.05 to 0.1 is obtained.

7. The process of Claim 6, wherein the etherification agent is sodium monochloracetate.

8. The process of Claim 6, wherein the etherification is 2-chloro-N,N-diethyl-ethyleneamine hydrochloride.

